

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 17, 1996		3. REPORT TYPE AND DATES COVERED Final: Oct. 1, 1992 - Feb. 29, 1996
4. TITLE AND SUBTITLE  Design Strategies for the Preparation of Polymeric Organic Superconductors			5. FUNDING NUMBERS  61103D 3484 RS	
6. AUTHOR(S) Prof. Charles W. Spangler, Northern Illinois University  Prof. John R. Reynolds, University of Florida			AFOSR-TR-96 0365	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Northern Illinois University Louden Hall 201, Circle Drive DeKalb, IL 60115			10. SPONSORING/MONITORING AGENCY REPORT NUMBER  F49620-92-J-0533	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  AFOSR/NC Building 410, Bolling AFB DC 20332-6448			11. SUPPLEMENTARY NOTES  19960726 064	
12a. DISTRIBUTION/AVAILABILITY STATEMENT  APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.				
13. ABSTRACT (Maximum 200 words)  Several copolymers were synthesized in which the known superconducting precursor bis-ethylenedithiotetrathiafulvalene, BEDT-TTF ("ET"), was incorporated as a formal repeat unit into aliphatic and aromatic polyesters as well as an aliphatic polyurethane. These polymers could be cast as optically quality thin films. All polymers could be oxidized to either monocation or dication forms in solution with antimony pentachloride, in which all the ET subunits had been oxidized. Et subunits could also be attached as pendant groups on a poly (methyl methacrylate) backbone with up to 60% incorporation. All of the polymers were thermally stable to above 200 degrees C., and were fully characterized by both DSC, TGA and GPC. Cyclic voltammetry clearly showed that the incorporated ET subunits were electroactive, with two redox peaks showing the successive formation of the radical cation and dication peaks. Room temperature DC conductivities for the polymer films before and after oxidative doping were obtained, with conductivities of the oxidized films generally falling between $10^{-6}$ to $10^{-4}$ S $\text{cm}^{-1}$ . Several attempts to incorporate TTF subunits into copolymer formulations proved to generally unsuccessful, although this research is continuing.				
14. SUBJECT TERMS  Superconductivity, BEDT-TTF, ET-Radical-cation, ET- Dication, Electroactive			15. NUMBER OF PAGES  16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT  UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE  UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT  UNCLASSIFIED	20. LIMITATION OF ABSTRACT	

## FINAL TECHNICAL REPORT

Title: "Design Strategies for the Preparation of Polymeric Organic Superconductors"

Inclusive Dates: October 1, 1992 - February 29, 1996

Grant Number: F49620-92-J-0533 (FY 93 URI/RIP)

Senior Research Personnel:

Professor Charles W. Spangler  
Department of Chemistry  
Northern Illinois University  
DeKalb, IL 60115-2862  
(815) 753-6880 (Phone)  
(815) 753-4802 (FAX)

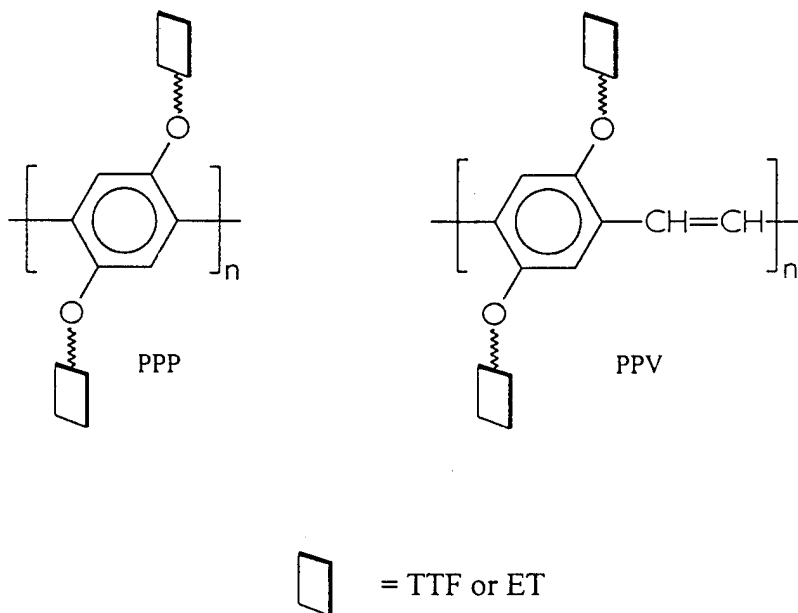
Professor John R. Reynolds  
Department of Chemistry  
University of Florida  
Gainesville, FL 32611  
(352) 392-9151 (Phone)  
(352) 392-9741 (FAX)

## *Outline*

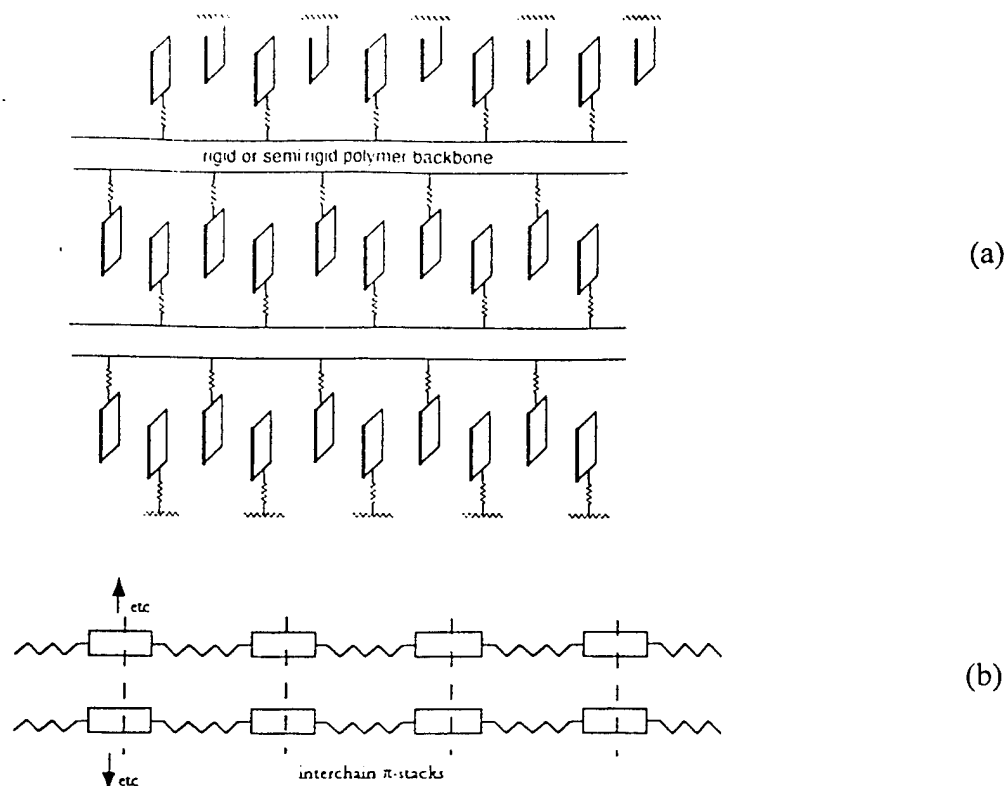
- I. Original Objectives
- II. Introduction
- III. Design Strategies for Polymers Containing BEDT-TTF Repeat Units
- IV. Design Strategies for Incorporation of BEDT-TTF Pendant Groups
- V. Attempted Synthesis of Polymers Containing TTF Subunits
- VI. Characterization of Copolymers Containing BEDT-TTF Repeat Units
  - A. GPC Results
  - B. Thermal Analysis
  - C. Cyclic Voltammetry
  - D. Optoelectrochemistry
  - E. Conductivity
- VII. Summary

## I. Original Objectives

The original objectives of this project were to develop design strategies for the synthesis of the first organic polymeric superconductors. We initially proposed to synthesize rigid-rod type polymers such as poly[p-phenylene] and poly[p-phenylene vinylene] with pendant groups containing known superconductor moieties such as tetrathiafulvalene (TTF) and bis-ethylene-dithiotetrathiofulvalene (BEDT-TTF or "ET").



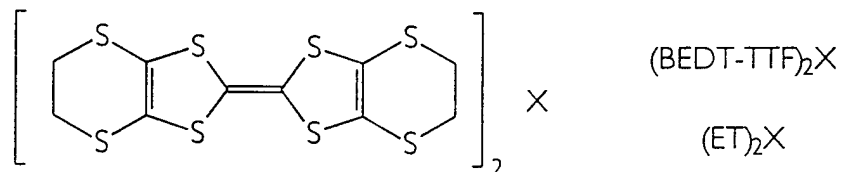
Both TTF and ET have been studied for potential superconducting behavior at low temperatures for the past 20 years, with much of the research centered around the electrocrystallized salts of these donor molecules with the stoichiometry  $D_2X$ .<sup>1</sup> However, the relatively low superconductivity onset temperatures ( $T_c$ ), coupled with the fragility of the electrocrystallized materials, has been a deterrent to their development and application. Thus it was proposed that if these moieties could be induced to form ordered intermolecular arrays while attached to stable, processible polymer backbones, then superconductivity in organic polymers might be achievable. In addition, incorporation of ET or TTF moieties into the backbone of a polymer (main-chain incorporation), separated by flexible spacers, might also offer an alternative approach to achieving the desired interchain  $\pi$ -stacks. Model representations of these two complementary approaches are illustrated in Figure 1.



**Figure 1.** Model structures for potential polymer superconducting arrays: (a) rigid-rod polymer with ET or TTF pendant groups; (b) main-chain copolymer incorporation of ET or TTF groups.

## II. Introduction

A large percentage of known superconductors have focused on electrocrystallized salts such as  $(\text{BEDT-TTF})_2\text{X}$ , where X represents a large family of counter anions.<sup>2</sup>

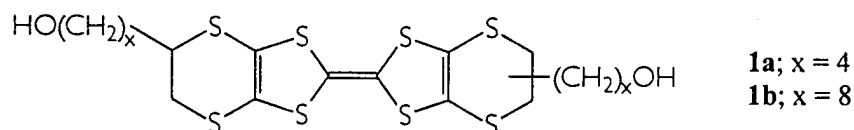


Exhaustive studies of this system from 1986 to the present have greatly enhanced the understanding of crystal packing of both ET and X upon  $T_c$  and has resulted in higher temperature superconductors.<sup>3</sup> Even a cursory reading of the voluminous literature on  $(\text{ET})_2\text{X}$  superconducting salts reveals that structure-property relationships are both extremely important to the design of high  $T_c$  organics and extremely difficult to generalize. One of the problems in electrocrystallization is that it is not possible to rationally control the nanostructure of the materials formed. Our approach to superconducting polymer design has been two-fold: (1) by using rigid-rod polymer backbones

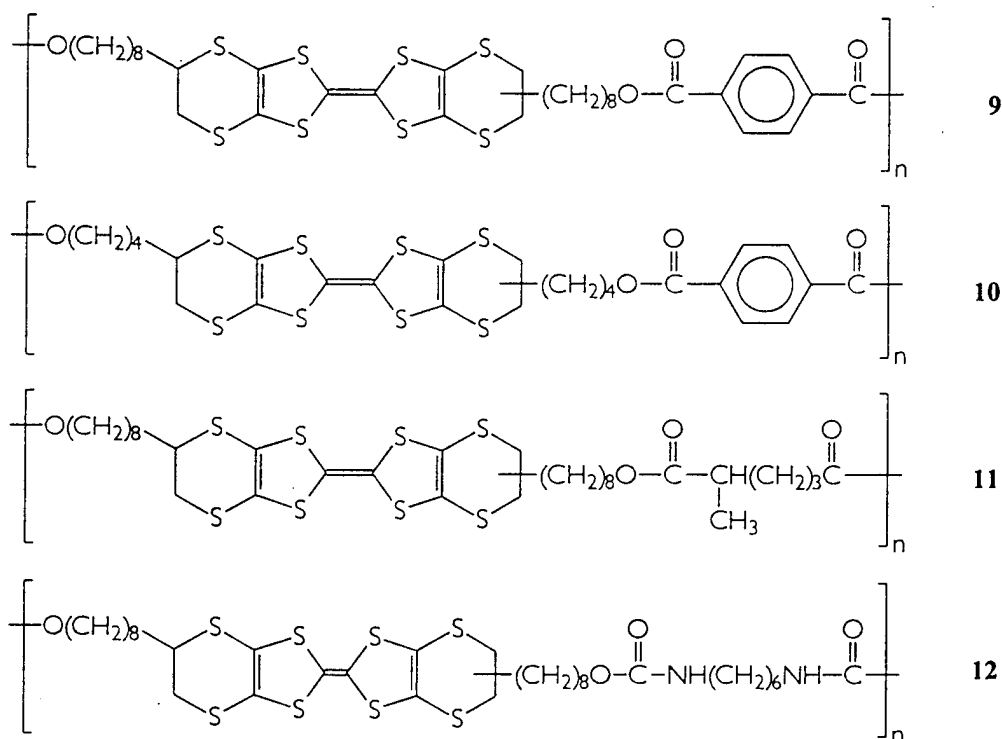
as templates for TTF or ET donor group self-assembly in interchain ensembles, and (2) incorporating ET moieties as formal main-chain copolymer repeat units alternating with flexible spacers which would allow potential main-chain intermolecular  $\pi$ -stacking. The design and synthesis of representative polymers from both of these classes are described in the following sections.

### III. Design Strategies for Copolymers Containing BEDT-TTF Repeat Units

ET monomers containing two polymerizable alcohol functionalities and variable-length spacers are accessible through modification of the standard synthesis of the parent *via* triethylphosphite

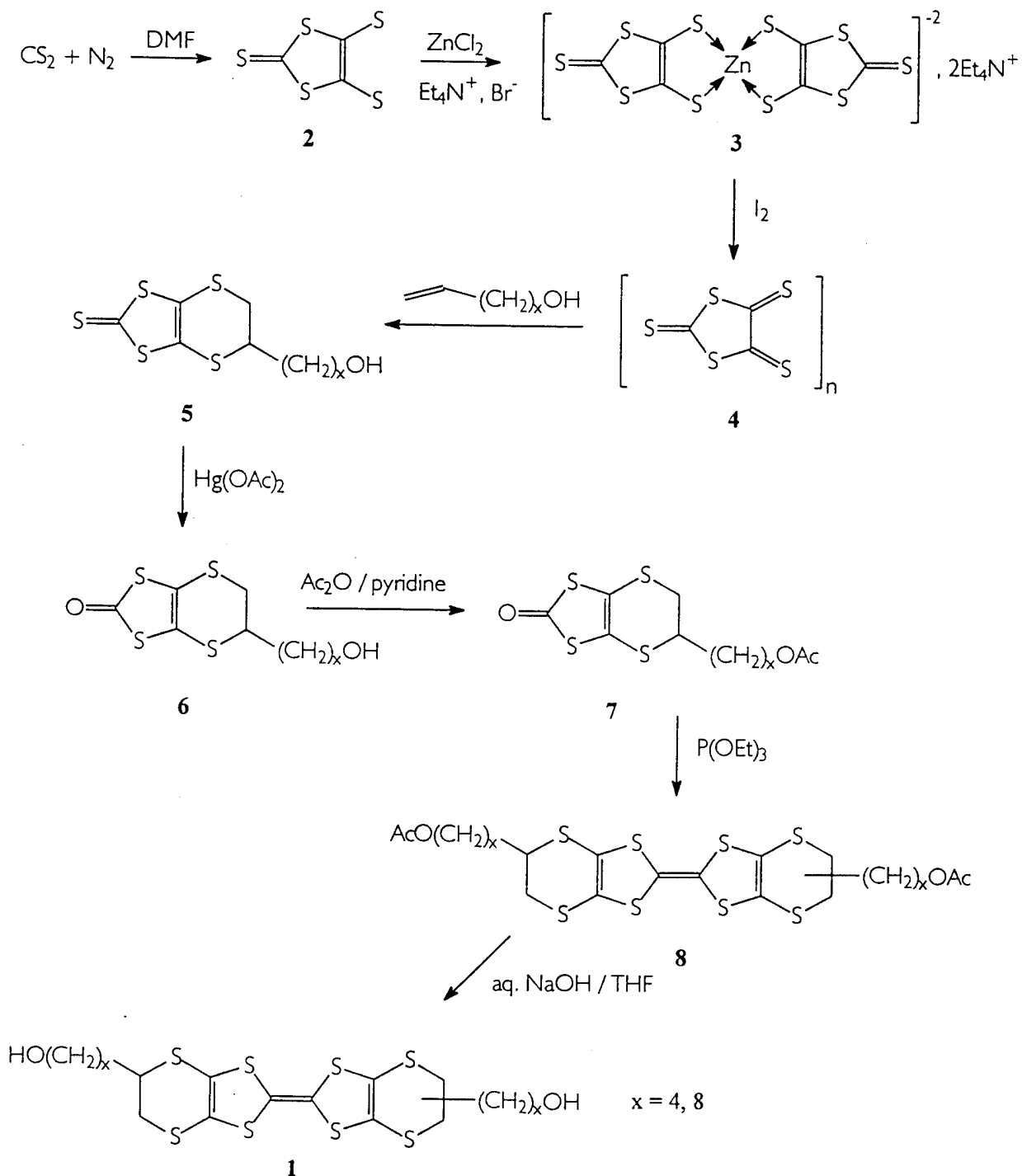


coupling. The synthesis of these monomers is outlined in Scheme 1. Both monomers are obtained in good yield and are obtained as a mixture of *cis* and *trans* isomers. No effort was made to separate these isomers prior to polymerization since it was postulated that inclusion of both subunits in the polymer backbone would yield amorphous polymer films with enhanced processibility. Four copolymers were synthesized in good yield from the ET-diol monomers:

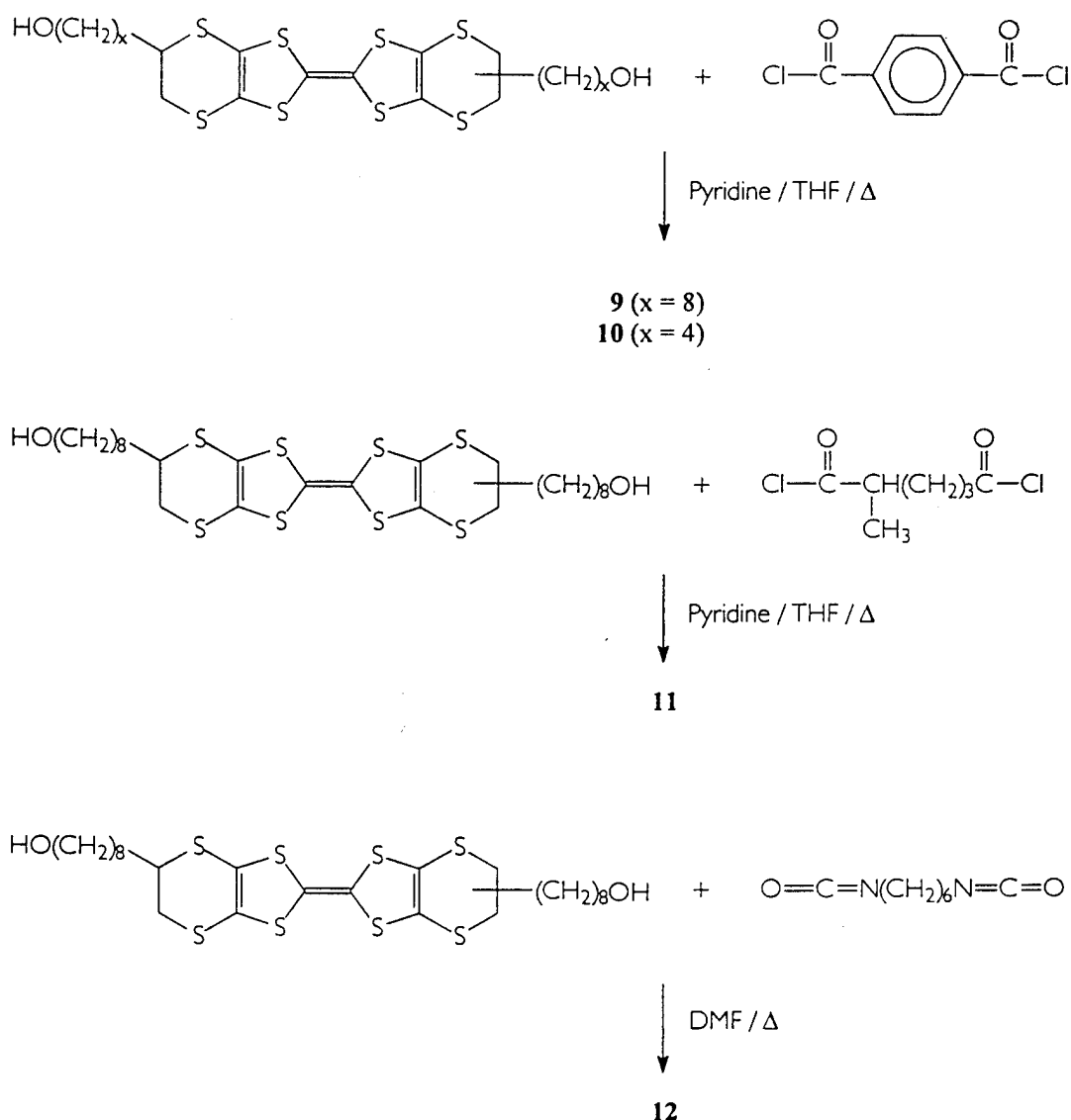


The syntheses of these copolymers are outlined in Scheme 2. The polymers could be cast as thin transparent films, and were characterized by gel permeation chromatography (GPC) to obtain  $M_n$  and  $M_w$ , thermal gravimetric analysis (TGA) and by differential scanning calorimetry (DSC). Cyclic

voltammograms (CV) were obtained for these polymers and showed the formation of two stable charge states, as does ET itself. These characterizations will be discussed in more detail in succeeding sections.



**Scheme 1.** Synthesis of  $\text{ET}[(\text{CH}_2)_x\text{OH}]_2$  monomers.

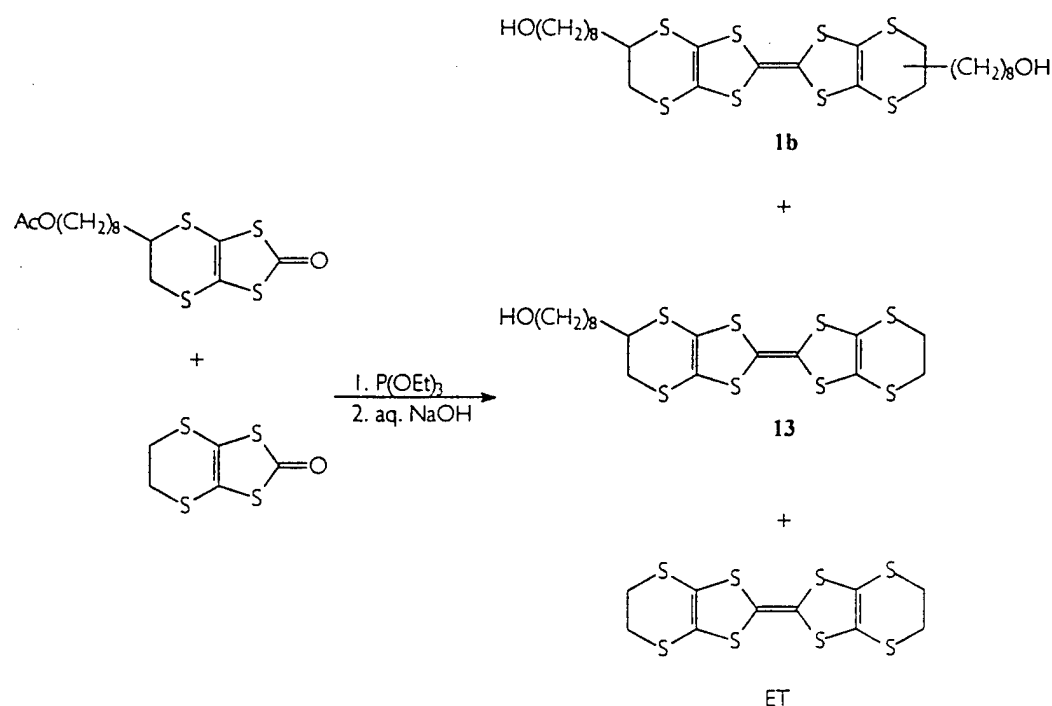


**Scheme 2.** Synthesis of ET-containing copolymers.

#### *IV. Design Strategies for Incorporation of BEDT-TTF Pendant Groups*

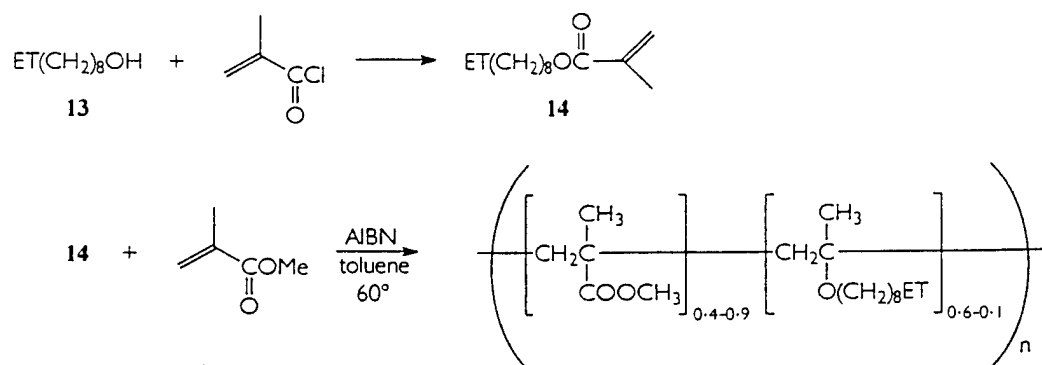
The success of incorporating nonlinear optical (NLO) chromophores as pendant groups attached to a polymethylmethacrylate backbone *via* flexible variable length spacers prompted us to employ this strategy to attach ET moieties to a PMMA backbone. An ET monomer containing one OH functionality could be obtained by a cross-coupling reaction followed by chromatographic separation, as outlined in Scheme 3:





**Scheme 3.** Synthesis of  $\text{Et(CH}_2)_8\text{OH}$ .

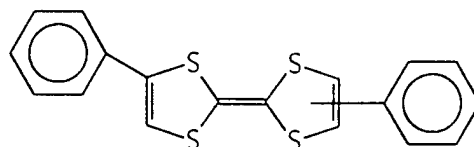
Reaction of **13** with methacryl chloride yielded monomer **14**, which could be copolymerized with methylmethacrylate in various ratios. Incorporation of up to 60% of the ET monomer into a random copolymer was accomplished with molecular weights approaching a maximum of 20,000. Attempts to polymerize pure ET monomer were unsuccessful.



### V. Attempted Synthesis of Polymers Containing TTF Subunits

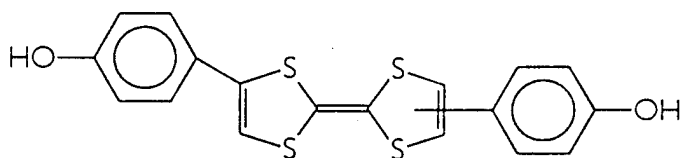
Difunctionalized TTF monomers are extremely difficult to synthesize and purify. Therefore, we took two different design approaches in preparing TTF derivatives for incorporation as either main-chain copolymers or as pendant groups. We initially synthesized a model compound which

incorporated two phenyl substituents, which demonstrated the efficacy of this approach. We have since synthesized two substituted diphenyl TTF units which contain functional groups capable of

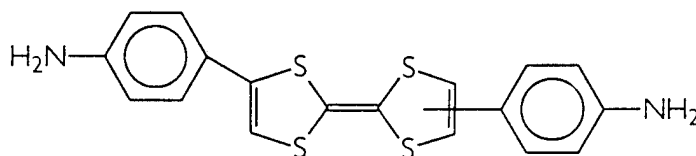


16

step-growth polymerization similar to that described in the previous sections for ET. These new monomers can now be converted to polyesters, polyamides and polyurethanes, and this phase of



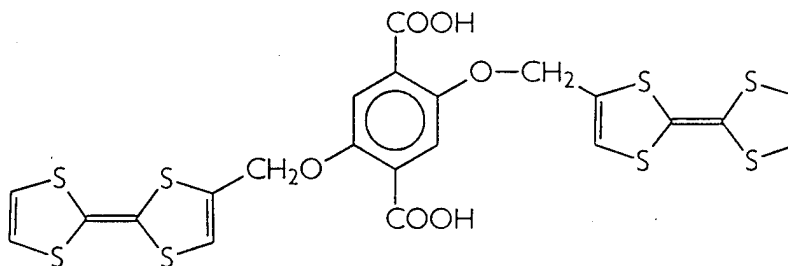
17



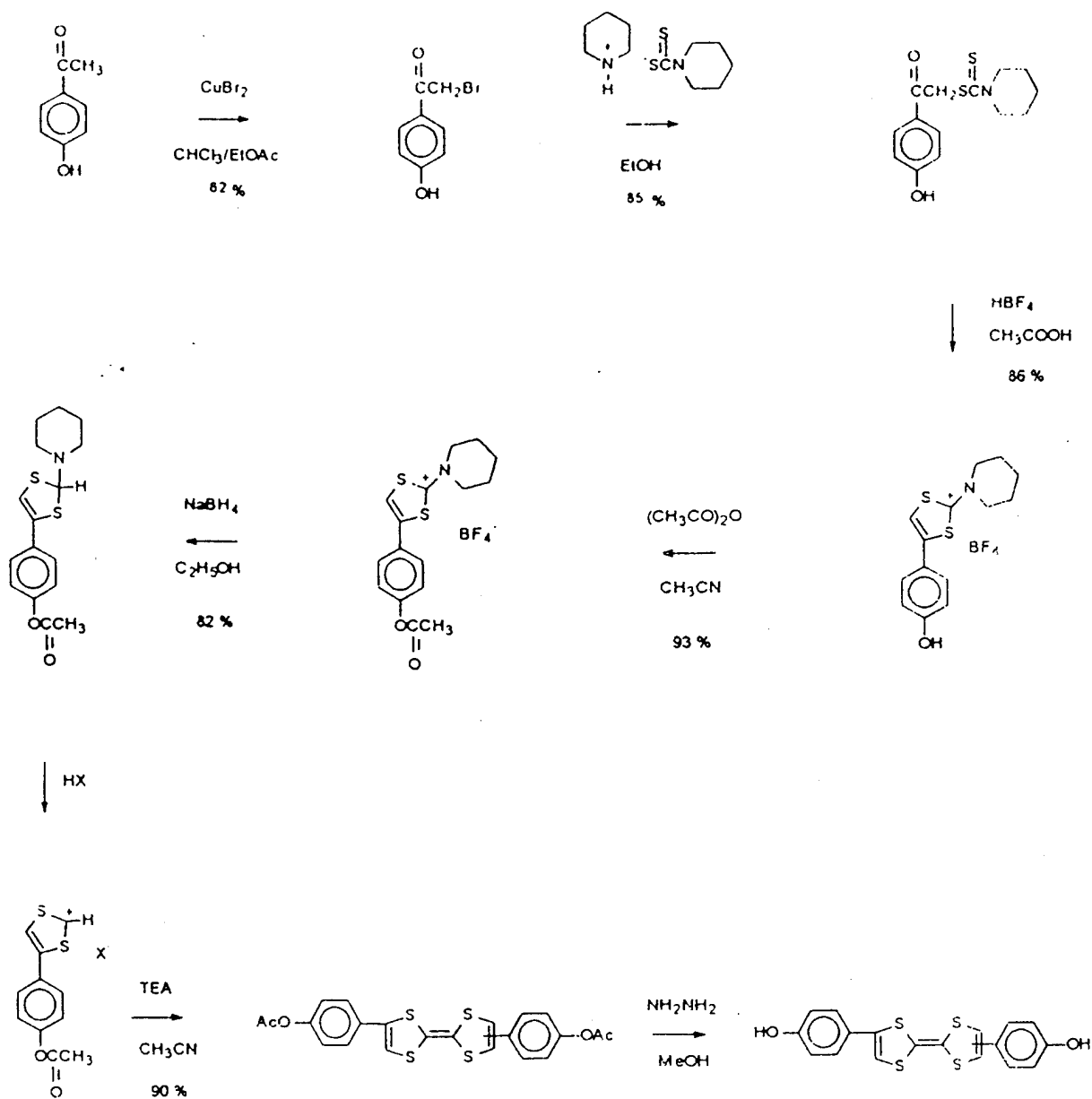
18

the research is still in progress and will be completed by a doctoral student (Mr. John Thurmond) who was recently awarded a Dissertation Completion Fellowship from Northern Illinois University to carry out the polymer design and synthesis.

We have also recently completed the synthesis of a monomer precursor with TTF subunits in a pendant orientation:

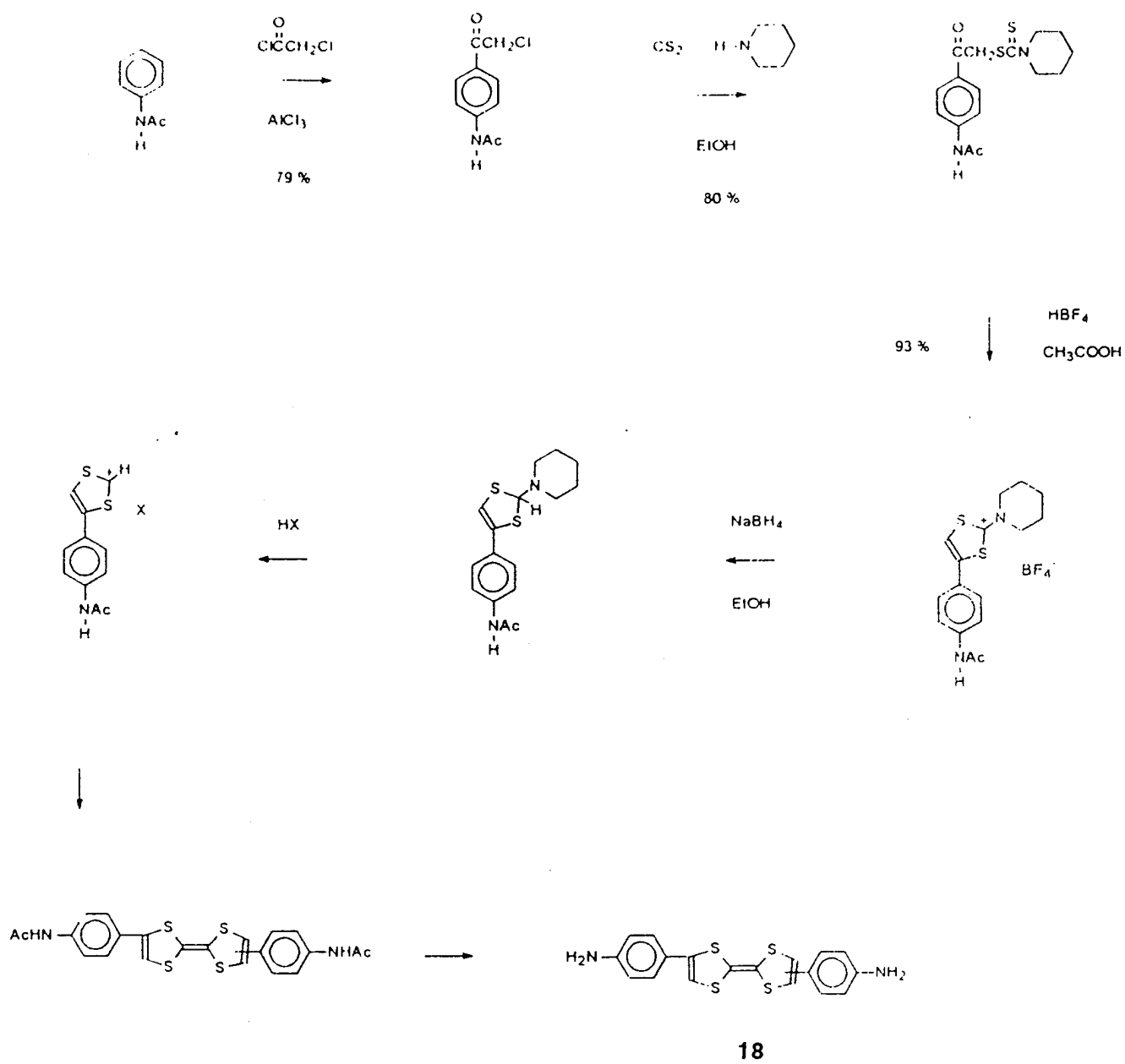


Mr. Thurmond will also study polyester and polyamide formation derived from this new monomer during the next year. The syntheses of the above monomers, and the projected polymerization processes, are illustrated in Schemes 4, 5 and 6.

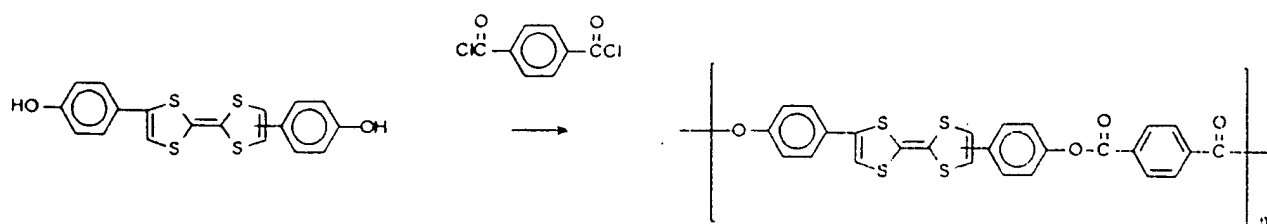


17

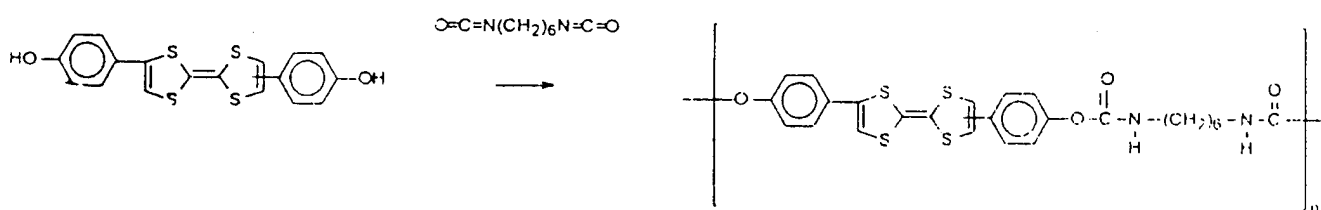
Scheme 4. Synthesis of TTF monomer 17



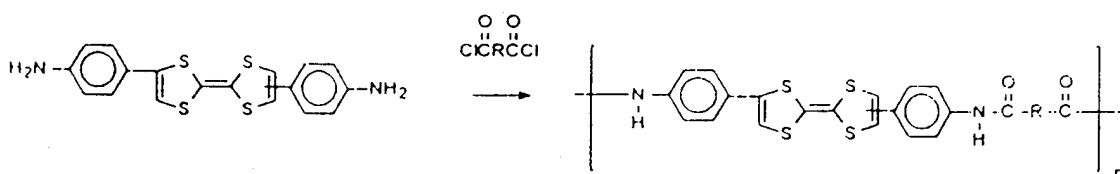
Scheme 5. Synthesis of TTF monomer 18



polyester



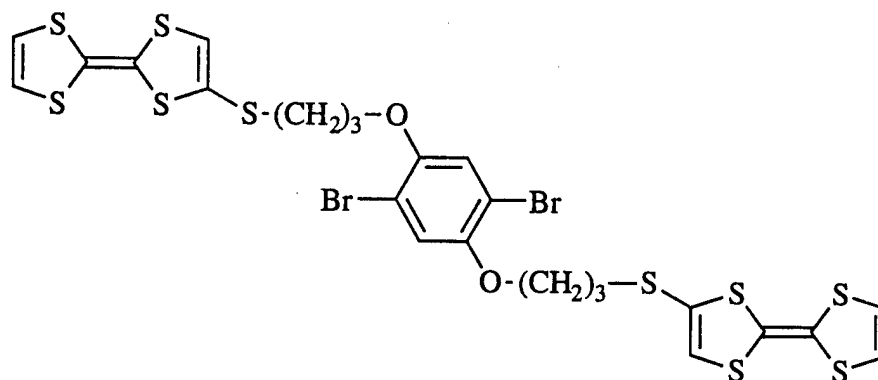
polyurethane



polyamide

Scheme 6. Synthesis of TTF main-chain polymers

A similar monomer was synthesized towards the formation of poly(*p*-phenylene) with pendant TTF units (see Scheme 7). Attempts to polymerize this monomer with Suzuki coupling failed.



20

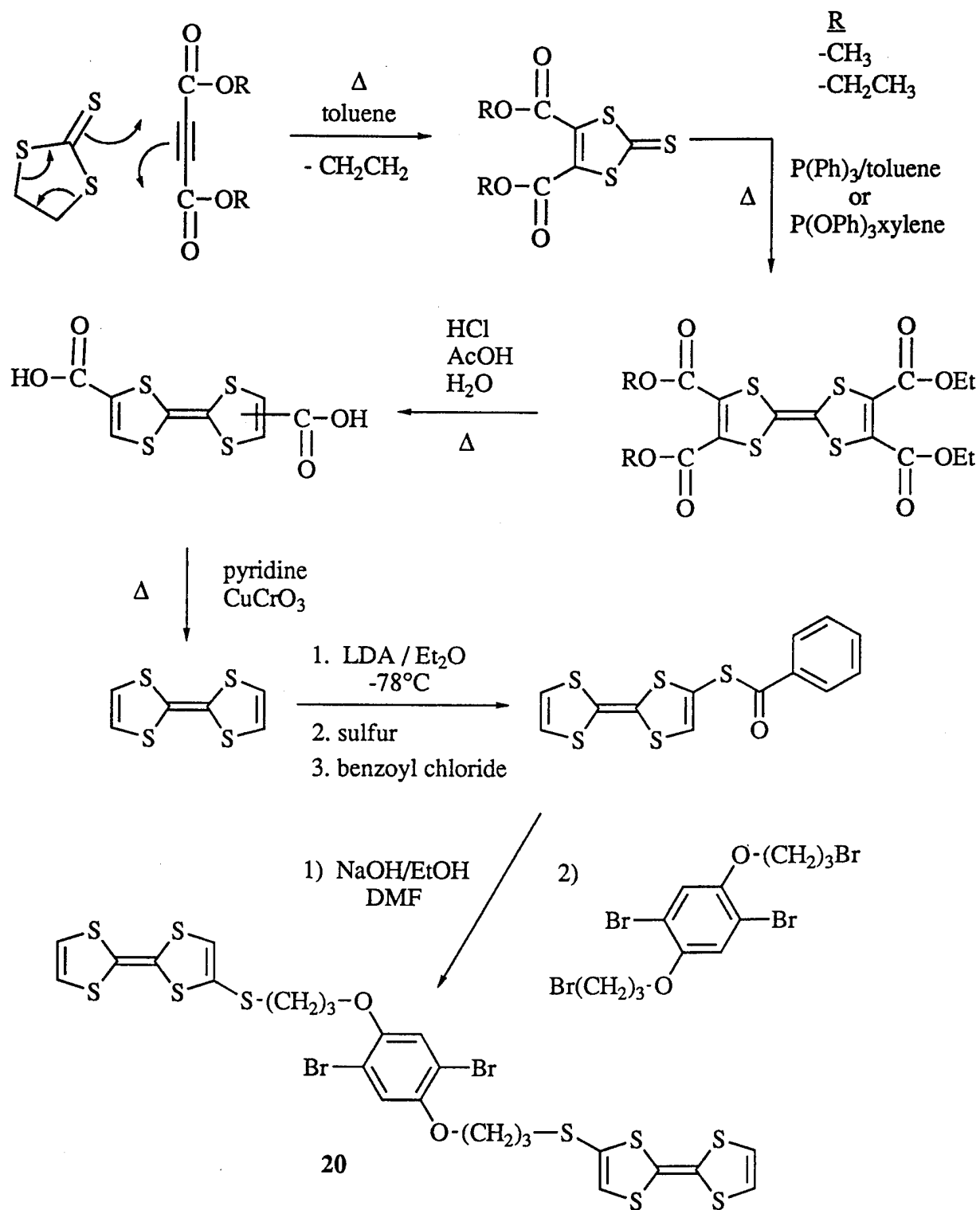
## VI. Characterization of Copolymers Containing BEDT-TTF Repeat Units

### A. GPC Results

Three of the four polymers, in THF solution, showed relatively broad polydispersities versus polystyrene standards. GPC traces of polymers **9**, **10**, **11** and **12** showed the presence of low molecular weight oligomers along with a high molecular weight tail. When exacting criteria were used to establish the baseline, i.e., the baseline established by pure solvent, the  $M_n$  appears low, while the  $M_w$  and  $M_w/M_n$  appear quite high (Table I). When a more liberal baseline was applied to define the dominant regions of the peaks the  $M_n$  was found to range from 3300 to 18,700.

Table I. GPC results in THF versus polystyrene.

Polymer	Baseline a			Baseline b		
	$M_w$	$M_n$	$M_w/M_n$	$M_w$	$M_n$	$M_w/M_n$
<b>9</b>	23200	3800	6.1	14300	7900	1.8
<b>10</b>	9700	500	19.3	9000	4300	2.1
<b>11</b>	44100	3200	13.9	29400	18700	1.6
<b>12</b>	40500	2200	18.7	9400	3300	2.8



Scheme 7. Synthesis of TTF-pendant dibromobenzene monomer.

## B. Thermal Analysis

Thermogravimetric analysis results are presented in Table II. All of the polymers are stable in nitrogen and in air to approximately 200°C. The lowest temperature decomposition was observed for polymer 10, which also showed the lowest molecular weight.

Table II. Thermogravimetric Analysis results.

Polymer	Heat ramp in nitrogen	Degradation Temperature (°C)		
		Onset	5% wt. loss	10% wt. loss
9	20°C / min.	217	268	276
10	-	198	224	245
11	5°C / min.	210	234	249
12	20°C / min.	214	259	264

Polymers 9, 11, and 12 were examined by DSC (Figures 2-5). The first heating scan of the aliphatic polyester 11 (5°C / min.) showed a variety of low energy exotherms from 20°C to 75°C, with a significant melt at 66°C. In the higher temperature region a melt may have been present at 140°C, but was buried in a series of sharp, low energy exotherms which may represent some reactive process. These effects were not seen in subsequent scans. No crystallization was observed in the cooling trace. The first heating of the aromatic polyester 9 showed two small transitions at 46°C and 57°C, followed by a strong melt at 148°C. Upon cooling at 5°C / min., two crystallization peaks were observed. The first, larger, crystallization occurred at 99°C, followed by a second exotherm at 77°C. In the second heating the major melting transition dropped slightly to 145°C. The small transitions observed in the first heat disappeared in the second heating trace. Following rapid quench (180°C to *ca.* 0°C in 2-5 seconds) some small features in this low temperature region reappear, possibly representing a glass transition from 50-57°C. The first heat of an annealed film (1 hour at 153°C, 48 hours at 80°C in vacuum) showed a similar low energy transition at 45°C. In addition to the melt transition at 145°C, the first heat of the annealed film of 9 revealed development of a second melt transition at 153°C, presumably due to a second, higher order packing arrangement. The cooling scan of the annealed sample was similar to that of the unannealed film, the thermal history having been destroyed. Major and minor crystallization peaks occurred at 98°C and 76°C, respectively. In the second heat, only one melt transition was observed, this at 141°C.



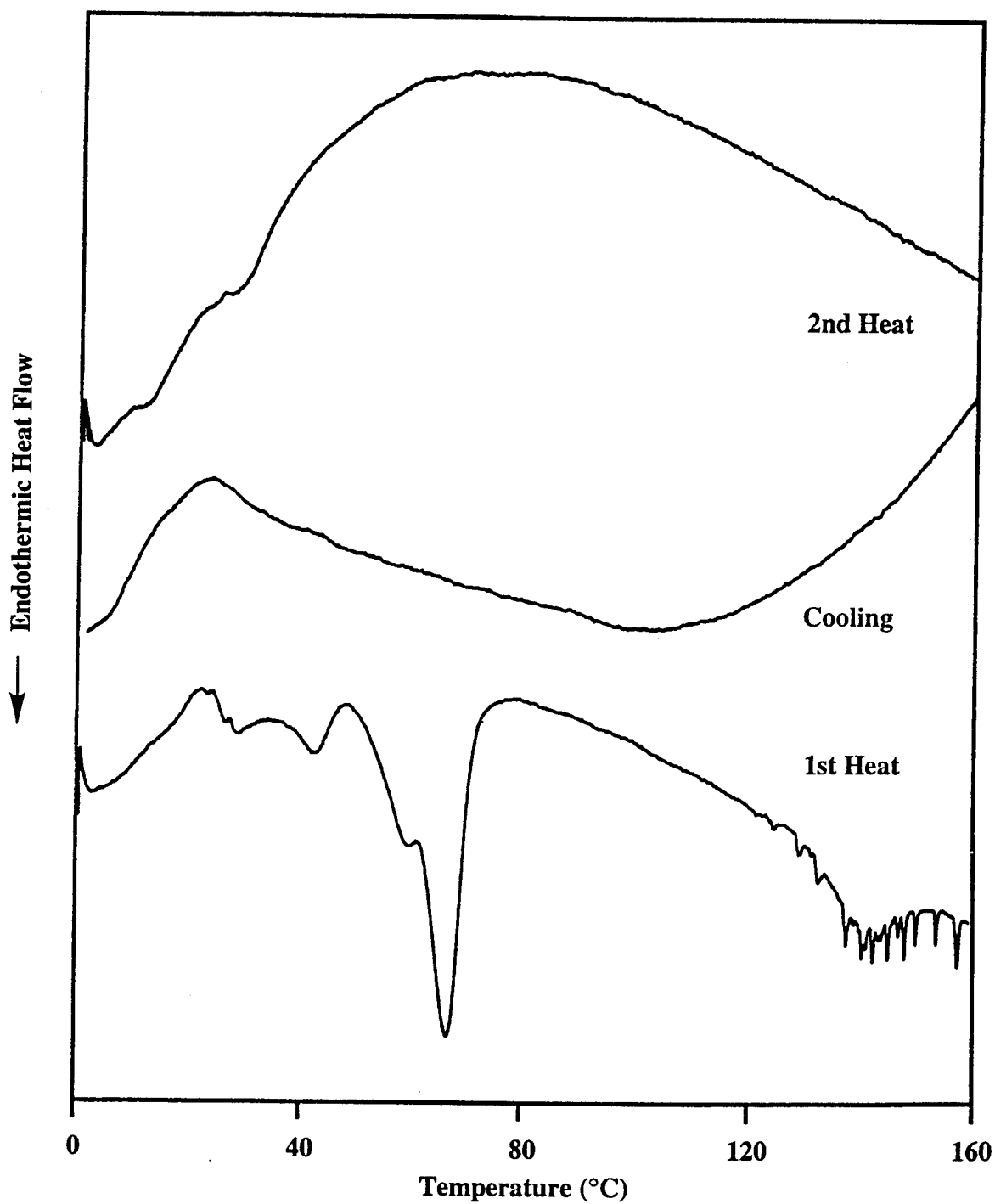
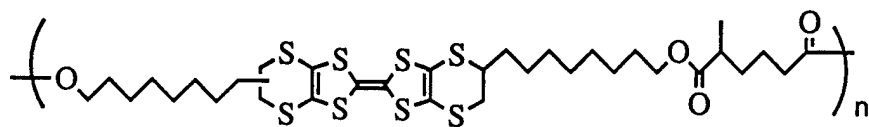


Figure 2. Differential scanning calorimetry traces of polymer 11. Heating and cooling at 5°C / minute.

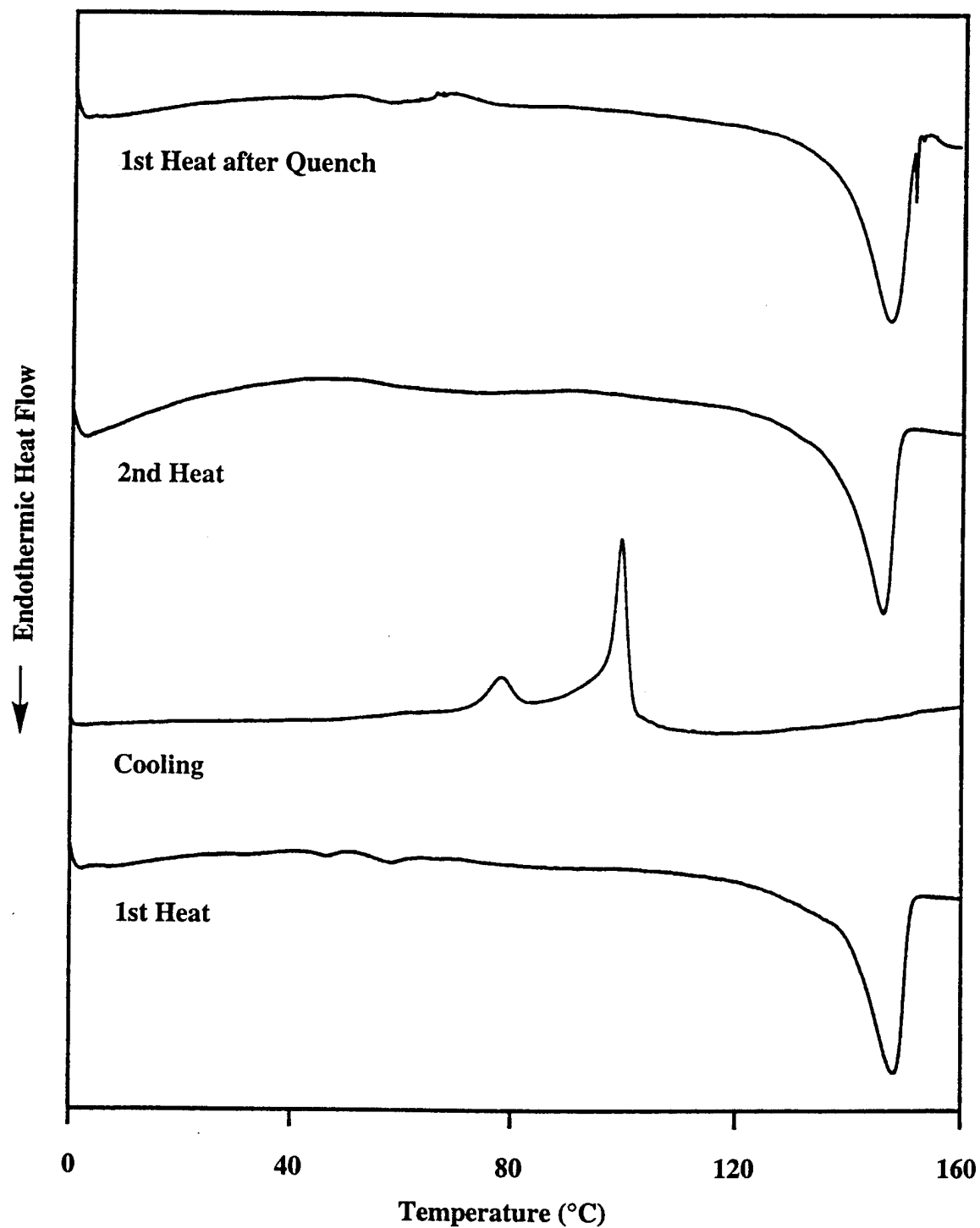
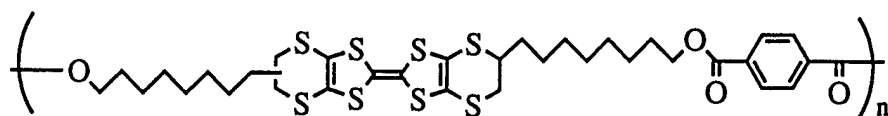


Figure 3. Differential scanning calorimetry traces of polymer 9. Heating and cooling at 5°C / minute; quench cooling 150°C to *ca.* 0°C in 2-5 seconds.

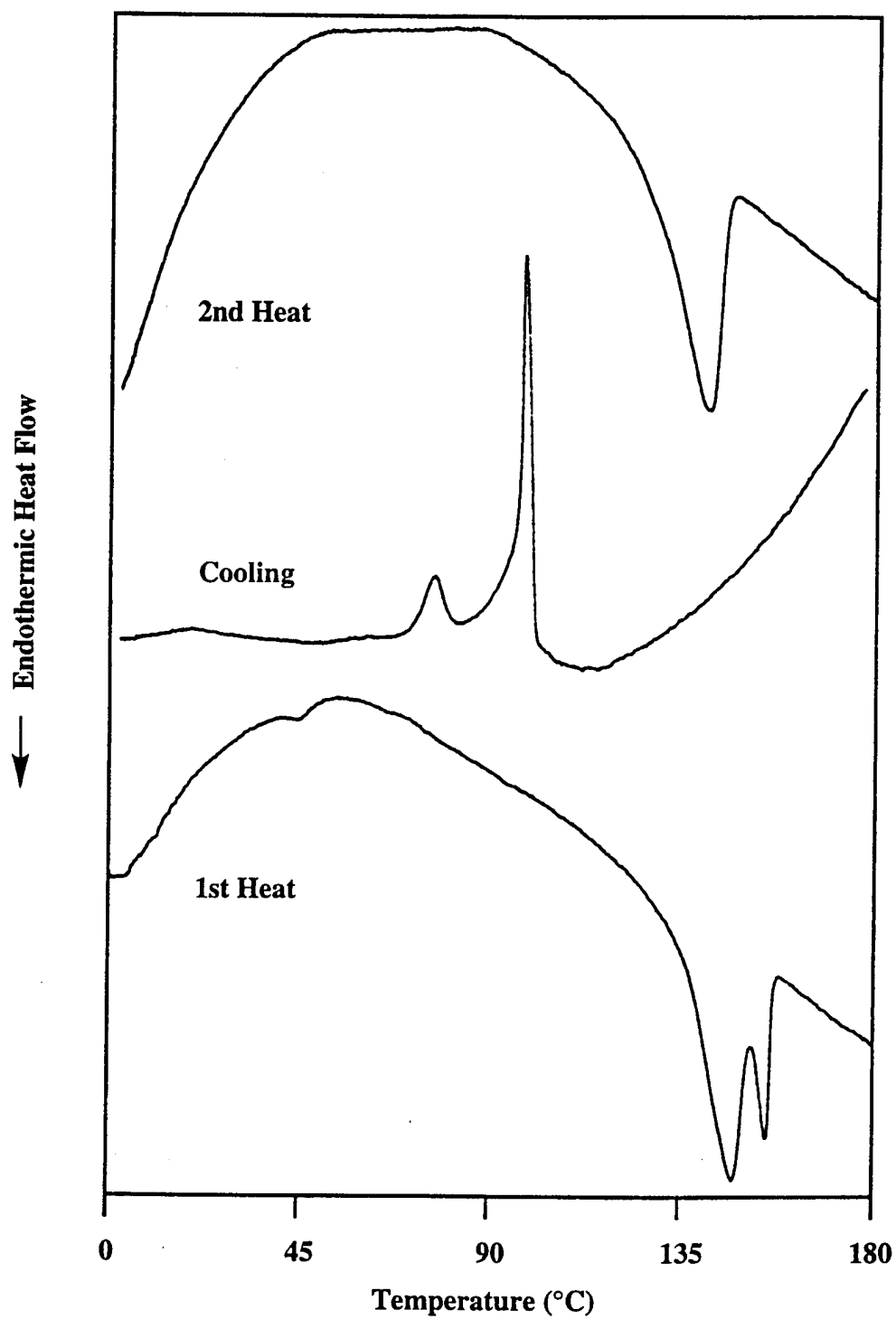
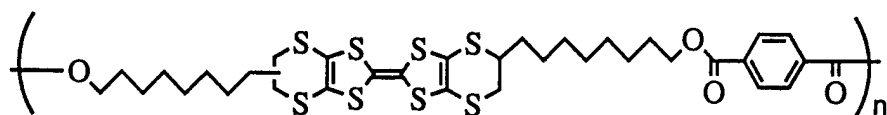


Figure 4. Differential scanning calorimetry traces of polymer 9. Prior to the first heating the sample was solution cast and annealed. Heating and cooling at 5°C / minute.

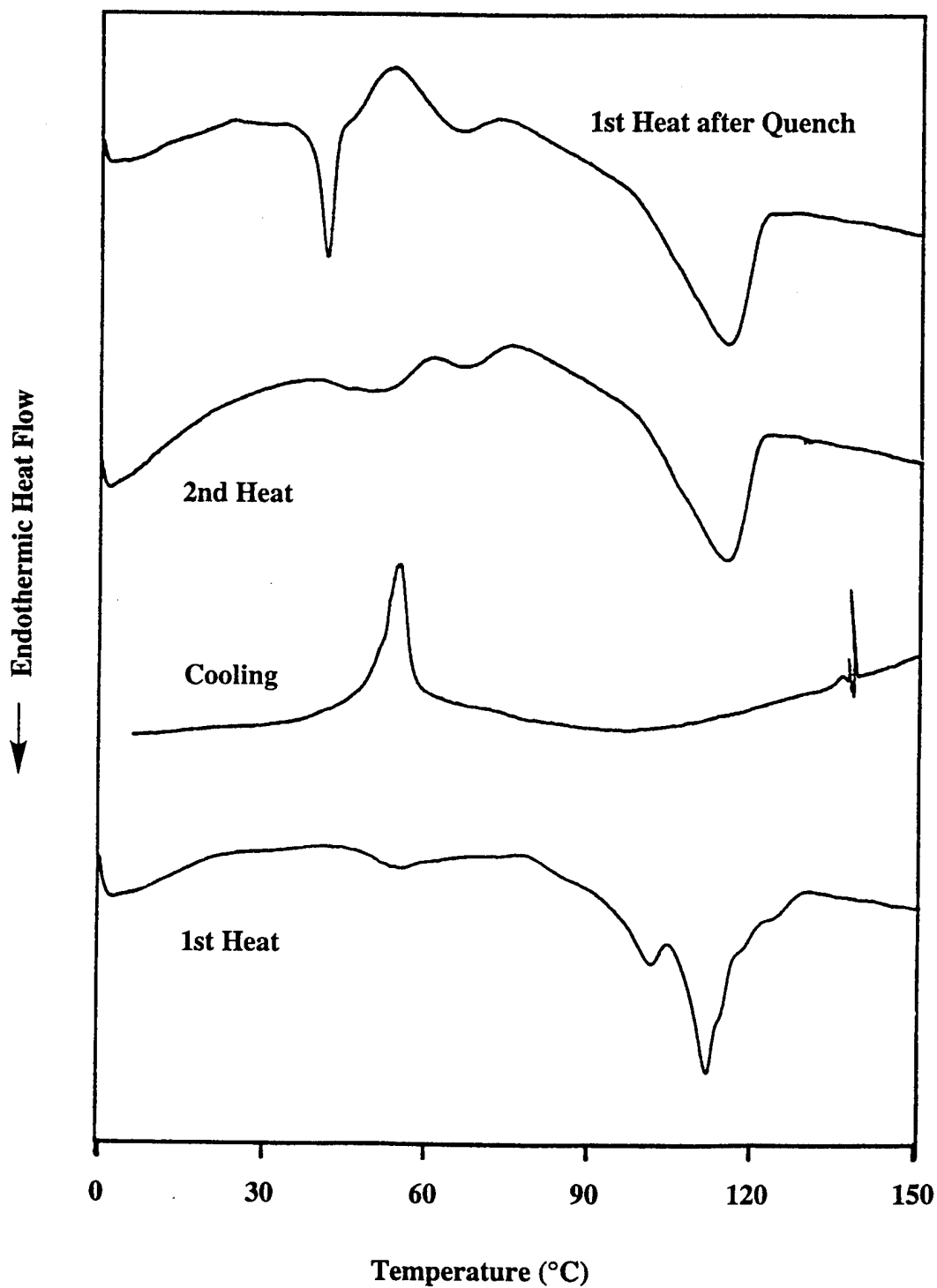
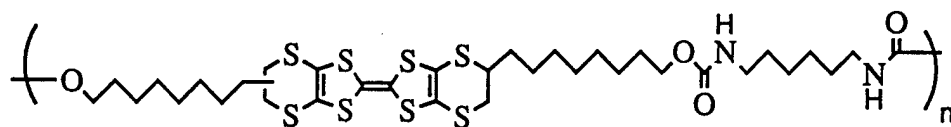


Figure 5. Differential scanning calorimetry traces of polymer **12**. Heating and cooling at 5°C / minute; quench cooling 150°C to *ca.* 0°C in 2-5 seconds.

The aliphatic polyurethane **12**, in the first heat, showed a low intensity broad exotherm, possibly a glass transition with onset at 44°C (peak at 54°C), and a larger broad exotherm from 77°C-139°C with a small peak at 101°C and a larger peak at 111°C. The cooling scan (excluding what is likely to be noise at *ca.* 138°C) showed a single sharp crystallization at 54°C. In the second heat one observes what could be interpreted as either two low intensity melts (48°C and 66°C) preceding a high intensity melt (114°C), or as a  $T_g$  (onset *ca.* 40°C) immediately followed by a crystallization (peak 60°C) and then by a single large melt (114°C). The latter case is supported by a post-quench cooling heat scan wherein the first endotherm was sharpened dramatically and the exotherm was found to coincide with the exotherm observed in the cooling scan. The polymers were viewed with cross polarizers on a hotstage optical microscope. No evidence was found for liquid crystallinity. Annealing resulted in enhanced birefringence at room temperature suggesting an elevated level of crystallinity.

### C. Cyclic Voltammetry.

Cyclic voltammetry of the polymers in dichloromethane solution confirmed that the redox behavior of the ET moiety remained intact and electroactive with its incorporation into the polymer backbone (Figure 6). The CVs of the ET-polyesters **9** and **11** were virtually indistinguishable from each other with first and second peak oxidation potentials  $E_{(ox)1} = 0.40$  V and  $E_{(ox)2} = 0.66$  V, respectively. These peaks illustrate formation of isolated radical cation and dication species of the donor units. Two reduction peaks are clearly present in these materials:  $E_{(red)2} = 0.30$  V and  $E_{(red)1} = 0.59$  V. The half wave potentials ( $E_{1/2}$ ) for these materials occur at 0.35 V and 0.62 V. The aliphatic polyurethane **12** CV is slightly less uniform, with some small shift in peak potentials:  $E_{(ox)1} = 0.43$  V,  $E_{(ox)2} = 0.67$  V,  $E_{(red)2} = 0.34$  V,  $E_{(red)1} = 0.56$  V; and some small shift in half wave potentials: 1st  $E_{1/2} = 0.38$  V, 2nd  $E_{1/2} = 0.61$  V. The aliphatic polyurethane also shows a shoulder on the anodic side of the first oxidation peak, at *ca.* 0.26 V, and a shoulder on the cathodic side of the second reduction peak, at *ca.* 0.23 V. As the potential was repeatedly cycled through the range of -0.1 V to 0.9 V, the 2nd reduction peak of this polymer gradually broadened and shifted to lower potential, *ca.* 0.28 V. Minor fluctuations aside, the polymers showed stable redox behavior in solution to 100 cycles.

The redox behavior of the aliphatic polyurethane **12** as a thin film, solution cast onto a platinum button, was also examined. In the first scan only one oxidation peak was evident. Relative to the first oxidation peak in solution, the peak was shifted to a high potential (0.78 V), and upon holding the recently cycled film at -0.1 V for several seconds, is reproducible. Presumably this phenomenon represents an initial migration of electrolyte into the polymer film

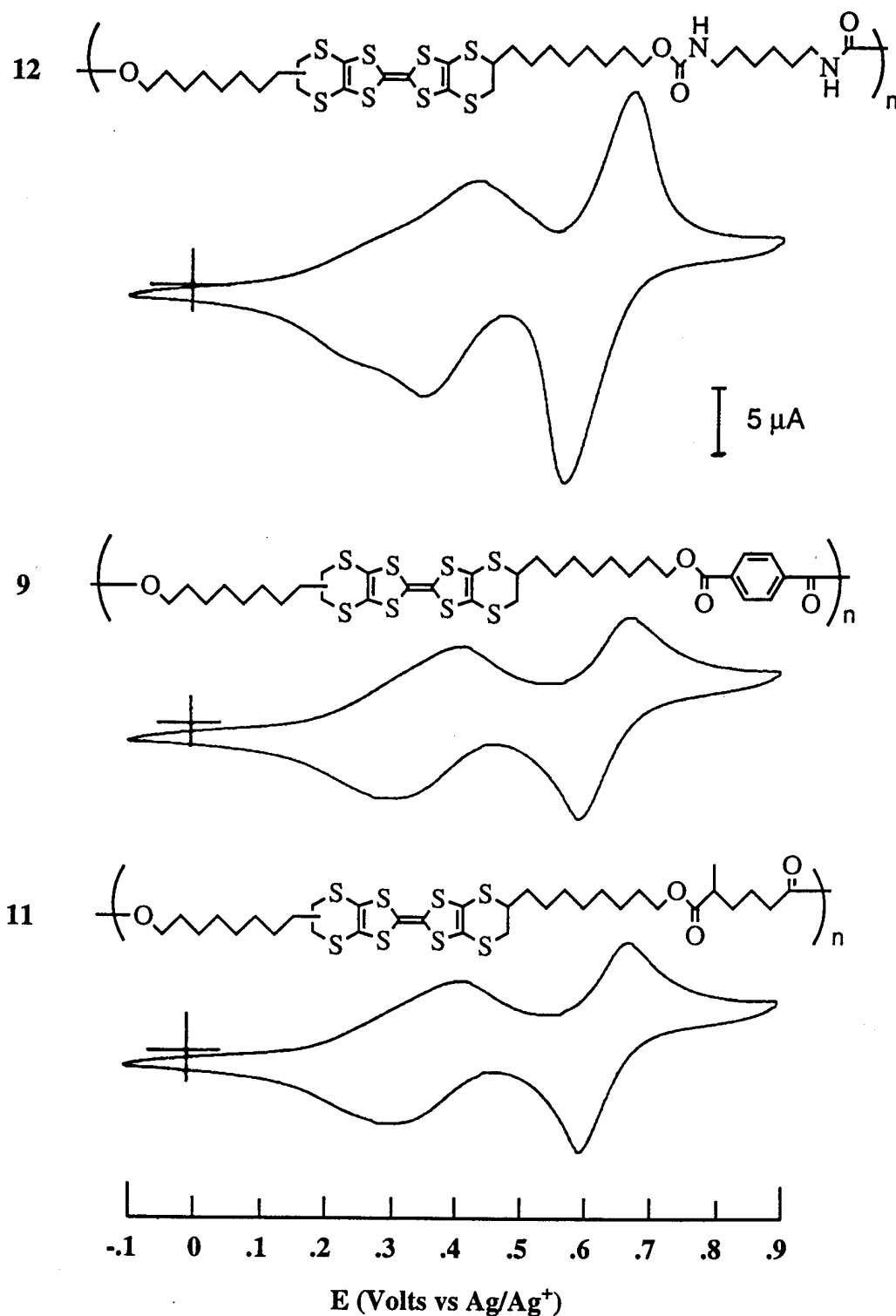


Figure 6. Cyclic voltammograms of ET containing polymers 9, 11 and 12. The CV's represent the 2nd scan of a room temperature 1 mM solution of the polymer in methylene chloride, 0.1 M in tetrabutylammonium perchlorate (TBAP) at a scan rate of 100 mV/sec.

to serve in charge balance. Following this initial loading of the polymer, two oxidation and two reduction peaks appear. With the exception of the second oxidation peak, the peaks for the urethane film are considerably shifted from their solution positions. The first oxidation peak occurs at higher potential,  $E_{(ox)1} = 0.49$  V, while the reduction peaks are shifted to lower potential:  $E_{(red)2} = 0.11$  V,  $E_{(red)1} = 0.46$  V. The half wave potentials for the first and second redox processes are 0.30 V and 0.56 V, respectively. The predominant charge transfer processes occur at  $E_{(ox)1}$  and  $E_{(red)2}$ , as noted by the enhanced intensity of these peaks relative to  $E_{(ox)2}$  and  $E_{(red)1}$ . Thus, while the ET moiety in the polymer film retains redox activity, it engages in the process with increased difficulty, and with successive scans passivates the electrode, possibly resulting from polymer decomposition or dissolution at the electrode surface.

#### *D. Optoelectrochemistry*

Upon confirmation that the aliphatic polyurethane **12** had retained redox behavior as a film, a thin film of was prepared on ITO glass and the electronic spectra determined as a function of applied potential vs Ag wire (Figure 7). The neutral film showed two absorption maxima, one at 390 nm and a lower intensity band at 520 nm. These peaks, due to intramolecular electronic transitions, showed a dramatic increase in intensity when scanned up to a potential of 0.4 V, as well as a slight blue shift—a possible reflection of increased interactions between the ET moieties within the solid film.<sup>4</sup> The  $\lambda_{max}$  at 390 nm, following its initial increase in intensity at 0.4 V, gradually decreased in strength with continued increase in applied potential. As film oxidation progressed a new broad band grew in, extending from the top of the visible region into the near IR (ca. 600 - 1600 nm) with  $\lambda_{max}$  shifting from 920 nm down to 830 nm over the applied potential range of 0.4 V to 0.9 V.

#### *E. Conductivity*

Films used for conductivity studies were cast from hot concentrated solutions of the polymers in 1,1,2,2-tetrachloroethane. The clear orange films obtained were very pliable, tough and free standing after drying in a nitrogen stream. A slight decrease in toughness occurred following two days of drying under vacuum at 65°C, presumably due to the loss of plasticization by solvent. As none of the polymers were soluble in acetonitrile, doping was achieved by soaking the adhered films in a saturated solution of  $FeCl_3$  in acetonitrile for 10 minutes. The degree of doping or depth of dopant penetration was not determined, although upon doping all orange color was lost; the films became black and opaque. Room temperature DC conductivities for the three polymers **9**, **11** and **12** obtained by two probe resistance methods varied by two

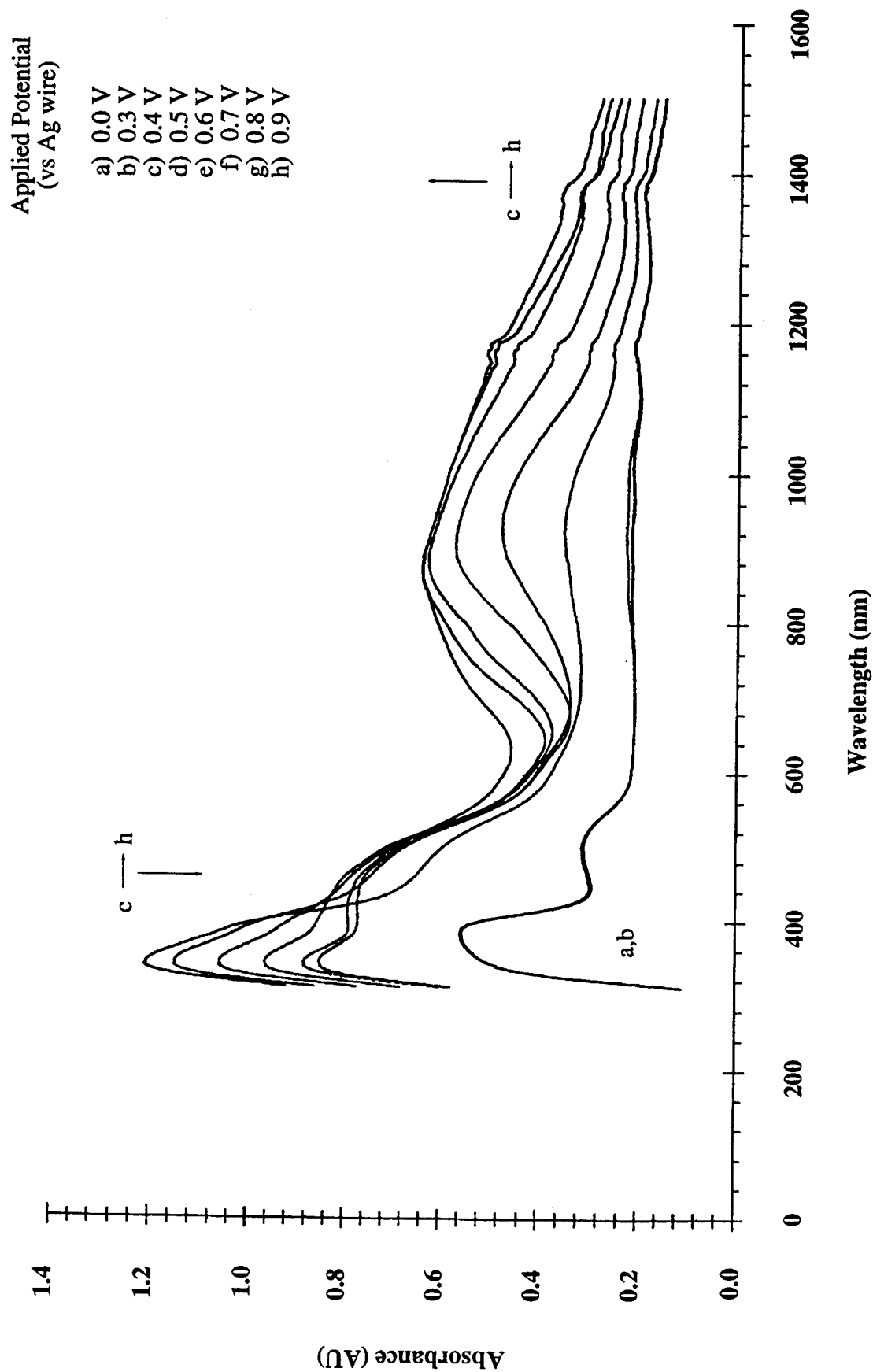
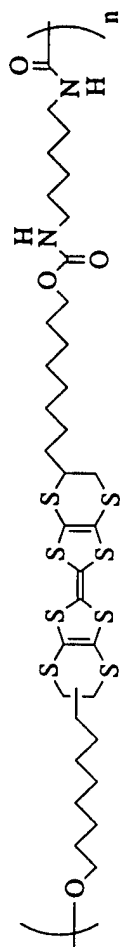


Figure 7. Optoelectrochemical spectra of **12** as a thin film solvent cast on ITO glass, switched in a 0.1 M tetrabutylammonium acetonitrile solution.



orders of magnitude, but were generally low. The aliphatic polyurethane had the highest conductivity,  $1 \times 10^{-4} \text{ S cm}^{-1}$ . The aliphatic polyester showed a conductivity of  $6 \times 10^{-5} \text{ S cm}^{-1}$ , and the aromatic polyester a conductivity of  $4 \times 10^{-6} \text{ S cm}^{-1}$ . Greater control of doping should result in conductivity enhancements. Doping the film with excess  $\text{FeCl}_3$  prior to casting gave a gray-green insulating material. Annealing the films should likewise enhance conductivity by increasing ET ordering within the polymer matrix. However, films which were annealed prior to doping were very resistant to doping; films which were annealed in vacuum after doping decomposed.

Films were also doped with iodine *in situ*. The polymers doped poorly at  $25^\circ\text{C}$ . At  $55^\circ\text{C}$  doping proceeded smoothly, although initial conductivity enhancements were partially reversible at 4-5 torr. Table III lists conductivity values measured at room temperature after no further changes in conductivity were observed in samples exposed to vacuum. Stretch oriented samples were drawn by hand at room temperature. Conductivity in an iodine doped sample of 11 which was stretch oriented 500% was found to be one order of magnitude greater in the direction perpendicular the stretch axis. FT-IR results based on the method of dichroic ratios<sup>5</sup> shows the ET moieties in this sample to be oriented  $45^\circ$  to the stretch axis.

Table III. Two Probe DC Conductivity Data

Polyester (9)	Dopant	L (cm)	A [(cm) <sup>2</sup> ]	R (W)	s (S cm <sup>-1</sup> )
unoriented film	$\text{FeClO}_4$	0.440	$6 \times 10^{-4}$	$4.0 \times 10^8$	$2 \times 10^{-6}$
unoriented film	$\text{I}_2 / 25^\circ\text{C}$	0.110	$4 \times 10^{-3}$	$8.5 \times 10^7$	$3 \times 10^{-7}$
Polyester (11)	Dopant	L (cm)	A [(cm) <sup>2</sup> ]	R (W)	s (S cm <sup>-1</sup> )
unoriented film	$\text{FeClO}_4$	0.310	$2 \times 10^{-3}$	$3.2 \times 10^4$	$5 \times 10^{-3}$
$0^\circ$ to 500% stretch axis	$\text{I}_2 / 25^\circ\text{C}$	0.335	$5 \times 10^{-4}$	$5.6 \times 10^9$	$1 \times 10^{-7}$
$0^\circ$ to 500% stretch axis	$\text{I}_2 / 55^\circ\text{C}$	0.335	$5 \times 10^{-4}$	$4.1 \times 10^7$	$2 \times 10^{-5}$ (a)
$90^\circ$ to 500% stretch axis	$\text{I}_2 / 55^\circ\text{C}$	0.275	$3 \times 10^{-4}$	$1.8 \times 10^6$	$5 \times 10^{-4}$ (a)
Polyurethane (12)	Dopant	L (cm)	A [(cm) <sup>2</sup> ]	R (W)	s (S cm <sup>-1</sup> )
unoriented film	$\text{FeClO}_4$	0.333	$4 \times 10^{-3}$	$1.5 \times 10^5$	$6 \times 10^{-4}$
unoriented film	$\text{I}_2 / 25^\circ\text{C}$	0.275	$2 \times 10^{-4}$	$1 \times 10^{10}$	$1 \times 10^{-7}$
$0^\circ$ to 140% stretch axis	$\text{I}_2 / 25^\circ\text{C}$	0.230	$5 \times 10^{-4}$	$1 \times 10^{10}$	$5 \times 10^{-8}$ (b)
$90^\circ$ to 140% stretch axis	$\text{I}_2 / 25^\circ\text{C}$	0.190	$5 \times 10^{-4}$	$5.6 \times 10^9$	$7 \times 10^{-8}$ (b)

(a) Same sample. (b) Same sample.

## *VII. Summary*

Aliphatic diol monomers containing BEDT-TTF units were synthesized and polymerized by stepgrowth methods to obtain clear free standing polyester, polyamide and polyurethane films which maintain the redox behavior the the parent BEDT-TTF molecule. Similarly, two new diphenyl-TTF monomers have been prepared for the synthesis of polyesters, polyamides and polyurethanes which incorporate the BEDT-TTF moiety into the polymer backbone. Donor units have been appended as sidechain mesogens to terephthalic acid for the synthesis of polyamides and polyesters, and to methacrylate—from which copolymers with methyl methacrylate have been prepared.

### *Interactions/Transitions*

In June 1995, the PI (CWS) presented a seminar to the Hardened Materials Branch, MLPJ, Wright Labs, on the possibility that polaron-like or bipolaron-like charge states photogenerated by intense laser irradiation might have potential applications involving sensor or eye protection. Since the ET-containing polymers designed and synthesized in this study have very stable, highly absorbing charge states (both mono- and dication), several of these polymers were supplied to MLPJ along with the oxidation spectra to test as potential new optical limiters (MLPJ contact: Dr. Tom Cooper).

In January 1996, we entered into an agreement with Laser Photonics Technology to synthesize and supply them with ET-containing copolymers as well as the ET-diol monomer to evaluate as potential sensor and eye protectors *via* reverse saturable absorption (RSA). This research is being funded by the U.S. Army Tank-Automotive Command (TACOM contact: Mr. Robert Goedart) as an SBIR Phase I effort to develop new materials to protect army personnel from laser attack. The PI (CWS) is acting as both a subcontractor and consultant on this SBIR contract. We anticipate submitting a Phase II request by September 1996.

### *Personnel Supported*

#### *A. Northern Illinois University*

The following worked as post-doctoral research associates during the tenure of this program:

1. Dr. Tom J. Hall
2. Dr. Linfang Zhu

3. Dr. Ziqi Lu
4. Dr. Bing Lin

In addition, several graduate students (Mr. John Thurmond, Mr. Mingqian He, and Ms. Mamatha N.) participated in some aspects of the program, as well as several undergraduate research assistants (Mr. William Veldhuyzen and Mr. Hu Li).

#### *B. University of Florida*

1. Mr. Peter Balanda (graduate research assistant)
2. Mr. David Irvin (graduate research assistant)
3. Mr. Seungho Kim (graduate research assistant)
4. Mr. William Latham (undergraduate research assistant)

#### *New Discoveries, Inventions, or Patent Disclosures*

At the current time, no patent disclosures have been filed; however, we anticipate that if the ET polymers show promising optical limiting capability as a result of ongoing studies at Wright Labs or Laser Photonics Technology, a patent disclosure will be filed within the next year.

#### *Presentations/Publications*

1. L. Zhu, T. Hall, J. Thurmond, Mamatha N, and C. W. Spangler, "Studies Toward the Design and Synthesis of Superconducting Organic Polymers Incorporating TTF and BEDT-TTF Subunits," 50th Southwest Regional Meeting, American Chemical Society, Ft. Worth, Texas, November 1994.
2. P. B. Balanda, A. D. Child and J. R. Reynolds, "Towards the Synthesis of Highly Functionalized Poly(*p*- phenylene)s," 208th National Meeting, American Chemical Society, San Diego, CA, March 1995; *Polym. Prepr.* **1994**, 35(1), 257.
3. Mamatha N, J. Thurmond, T. J. Hall, L. Zhu, and C. W. Spangler, "Incorporation of TTF Subunits in Main-Chain Copolymers and in Pendant Models," 210th National Meeting, American Chemical Society, Anaheim, CA, March 1995; *Polym. Prepr.* **1995**, 36(1), 479.

4. C. W. Spangler, L. Zhu, T. J. Hall, P. B. Balanda and J. R. Reynolds, "Studies Toward the Design and Synthesis of Superconducting Organic Polymers: Main Chain Incorporation of ET Subunits," 210th National Meeting, American Chemical Society, Anaheim, CA, March 1995; *Polym. Prepr.* **1995**, 36(1), 605.
5. C. W. Spangler, L. Zhu, Z. Lu, M. He, P. Balanda and J. R. Reynolds, "Synthesis, Characterization and Oxidative Doping Behavior of Copolymers Incorporating BEDT-TTF Repeat Units," 211th National Meeting, American Chemical Society, Chicago, IL, August 1995; *Polym. Prepr.* **1995**, 36(2), 292.
6. C. W. Spangler and M. Q. He, "Multifunctional Conjugated Organic Materials Incorporating Stable Charge States," *Polymers and Other Advanced Materials*, P. N. Prasad, J. E. Mark, and T. J. Fai, Eds.; Plenum: New York, 1995, pp. 737-743.
7. C. W. Spangler and M. Q. He, "Charge-State Incorporation in Dithienylpolyenes and Thienylene Polyethylene Oligomers and Polymers," *Handbook of Organic Conducting Molecules and Polymers*, H. S. Nalua, Ed.; John Wiley & Sons: New York (in press).
8. C. W. Spangler and M. Q. He, "Design of New Copolymers for Photonics Applications: Incorporation of NLO-Active Chromophores with Well-Defined Conjugation Lengths," *Mat. Res. Soc. Symp. Proc.* **1995** (in press).

### References

1. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M.-H. Whangbo, *Organic Superconductors: Synthesis, Structure, Properties and Theory*, Prentice Hall: New York, 1990.
2. (a) K. Beckgaard, C. S. Jacobson, K. Martensen, H. J. Pederson and N. Thorup, *Solid State Commun.* **1980**, 33, 1119; (b) K. Beckgaard, K. Caneiro, F. B. Rasmussen, H. Olsen, G. Rindorf, C. Jacobson, S. Pederson and J. E. Scott, *J. Am. Chem. Soc.* **1981**, 103, 2440.

3. (a) A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. Stupka, D. Jung and M.-H. Whangbo, *Inorg. Chem.* **1990**, *29*, 2555; (b) J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. L. Pyrk, D. M. Watkins, J. M. Kommers, S. J. Buryshuk, A. V. Streitby Crouch, J. E. Schriber, D. L. Overmyer, D. Jung and M.-H. Whangbo, *Inorg. Chem.* **1990**, *29*, 3272.
- 4) Torrance, J.B.; Scott, B.A.; Welber, B.; Kaufman, F.B.; and P.E. Seiden, *Phys. Rev. B* **1979**, *19*, 730.
- 5) Siesler, H.W., *Adv. Polym. Sci.* **1984**, *65*, 2-73.